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Artificial weathering of creosote with water and oxygen

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ARTIFICIAL WEATHERING OF CREOSOTE WITH WATER AND OXYGEN

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

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Introduction

There are many experiments being carried on in the field of wood preservation, partially because of the variations in the toxicity of many preservatives. The commercial interest is along the lines of expense, since some preservatives have not proven satisfactory because after a short period of time attack by fungus and insects has set in.

The question of permanence includes the weathering of creosote and other wood preservatives, even if impregnation of the wood has been well done. Much of the preservative may be lost from the pores of the wood by the expansion and contraction of the wood from season to season. This has been studied somewhat by the various companies who produce wood preservatives. In this paper the effects of weathering alone will be considered.

The effects of weathering can be shown by toxicity tests on the weathered preservatives themselves. Nutrient-agar gels have been used for this purpose, even though they are not considered too reliable by many investigators. The wood block tests have been preferred by these investigators as they claim the results more nearly reproduce nature than the nutrient-agar gels. Since most toxicity tests have been run on gels, this study has used them to show the effects of water and oxygen on creosote.

The weathering of creosote may be divided into four factors; oxidation, leaching, evaporation, and the effects of the soil. The effects of heat, or evaporation, on the toxicity of creosote have been studied (2,3), and it was believed that the lower boiling hydrocarbons lost by this process caused a marked decrease in toxicity of the creosote.

The effects of soil have been studied by Weeks (9) in a series of controlled laboratory experiments.

This thesis is concerned chiefly with the effects of oxidation and leaching. These factors have been insufficiently investigated to produce conclusive evidence on their effects on the toxicity of creosote.

Since the other components of air are thought to have little effect on the toxicity of creosote, pure oxygen was used to study the oxidation of creosote. Tap water was used for the leaching, or water extraction, in order to duplicate more closely in the laboratory the conditions found in nature.

Historical

The first work was published on the effect of oxidation on the toxicity of creosote in 1940 (2). Using the process of oxidation in any oxygen bomb under high pressure, it was found that oxygen entered the nucleus or sidechains of the aromatic compounds causing the formation of phenols, alcohols, aldebydes, and carboxylic acids which were less toxic than their corresponding hydrocarbons. But an apparent contradiction was found when a hydroxyl group was added to a hydrocarbon that was not quite soluble enough to yield a solution which killed the test organism. The increase in solubility of the hydrocarbon was of greater importance than the decrease in toxicity due to the introduction of the hydroxyl group. They found little or no change in the toxicity of creosote due to oxidation. However, they did find a decrease in the toxicity as a result of evaporation.

In 1949 (3) another paper was published concerning the artificial weathering of creosote. Running air at atmospheric pressure at the rate of one liter per 51 seconds for a period of seven and one-half hours through creosote at 97°C., he found a marked decrease in the toxicity of the preservative. The factor of evaporation was not controlled, so the decrease in toxicity was due to both effects. No relationshippwas given between the amount of air and the decrease in toxicity.

The effects of evaporation of the low boiling hydrocarbons in creosote were studied by P.J.A. Losby and P.M.D. Krogh (4). After analyzing creosote impregnated wood that had been weathered for a period of five and one-half years, they found that 47% of the total creosote had been lost. 91% of the lost creosote had boiling points below 270°C., while practically none of the compounds boiling above 355°C. were lost.

Before this, Narayanamurti and Ranganathon (6) had found evaporation caused a marked decrease in the toxicity of creosote. They carried out experiments on the upper parts of fence posts which had been impregnated with creosote and allowed to weather for a period of time. Their results showed that the lighter fractions (compounds having the lower boiling points) of creosote were lost.

Baechler's work in 1949 (3) included the effects of water on creosote. By shaking small amounts of salt water with creosote, he thought he noticed a slight decrease in toxicity; however, since his methods were poor, he gave no definite proof of the effects of leaching on creosote. He believed that a longer period of leaching would lead to a marked decrease in the toxicity by the removal of cresylic acids and other toxic compounds that are appreciably soluble in water.

In contradiction to the implied belief of Baechler, Azevedo (1) found that the tar acids (phenols, creosols and naphthols) were not only less toxic than the corresponding hydrocarbons, but creosote as a wood preservative need not even contain them, as they have little or no effect on the toxicity.

In all toxicity tests the strain of fungus used is of importance. McCallon, Wellman and Wilcoxon (5) have stated that the steepness of slope of a toxicity curve depends more on the compounds being tested (in this case, creosote) than on the fungus itself. In this work, the fungus Lentinus Lepideus (Madesin 534) was used, because it is hard to kill by creosote, and because other workers in this laboratory were using it.

Experimental

A. Leaching

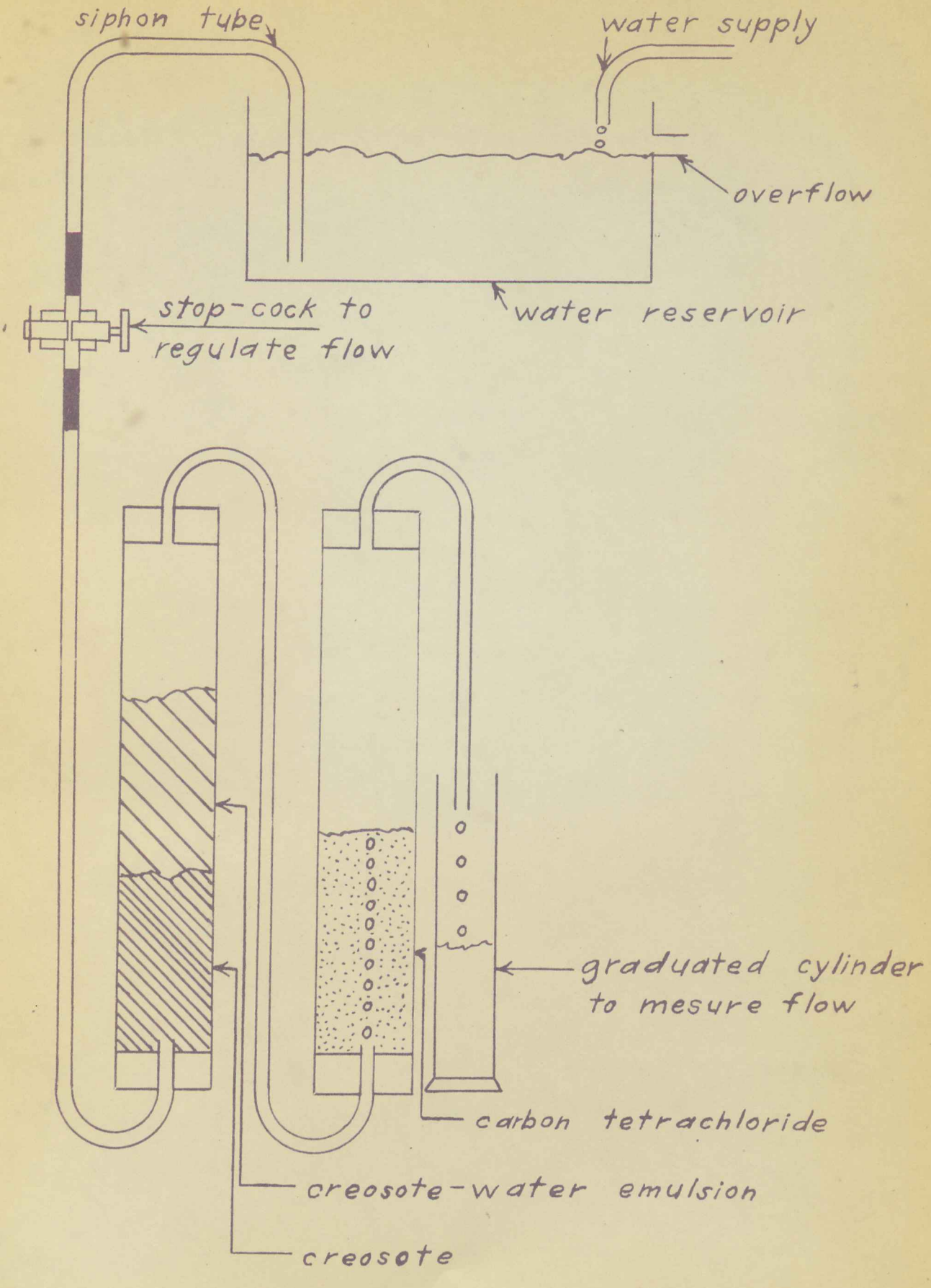
The testing was carried out using a medium residue Clairton creosote that was studied by Hathaway (7) and Weeks (9) in a number of distillation in toxicity experiments. The samples used were heated to 60°C. before withdrawal, so as to insure melting all of the components.

This creosote (300 g.) was placed in the bottom of a 4 ft.x 25 mm. glass column, as shown in figure 1, and tap water was bubbled up through the creosote. There were several problems in this process, since the creosote was only very slightly heavier than water. This meant that any unduly rapid flow of water caused a stable emulsion, and the flow had to be stopped until the emulsion broke.

In practice it was discovered that a flow of 80 to 100 ml. per minute gave an emulsion that could be controlled. As can be seen from the diagram in figure 1 (page 6),there was at all times an emulsion in the extraction tube. Care also had to be taken to exclude air bubbles, since these had distinct emulsifying tendencies. The third precaution needed was to start the flow only very slowly, so as to avoid sudden emulsification.

As can be inferred from the above, it was very important to have a steady, gas free flow of water. This was obtained by using a constant head storage tank held about 2 feet above the extraction tube. A constant stream of cold tap water (very hard, high in both calcium and magnesium ion content) was run into the tank at a 150 to 200 ml. per minute rate. The excess water ran off through an overflow, and hence a constant head of water was maintained. The dissolved gas in the tap water was largely re-

Leaching Apparatus



leased by running into the storage tank, but some gas continued to come out of the solution in the extraction inlet tube and caused some blockage of flow at various times, causing the flow rate to decrease. This flow blockage was caused chiefly by bubble formation in the stopcock. The line was easily freed, however, by temporarily disconnecting the apparatus and increasing the flow through the stopcock.

A column with carbon tetra chloride was placed in series with the extraction tube, in an attempt to recollect any material dissolved by the water. This re-extraction did not do as good a job as had been expected, as only 5 ml. were recollected out of the 81 ml. extracted by water.

The water was passed through this 300 g. sample of creosote for several weeks, until by calculation about 5000 l. of water were used, (the total volume each day was calculated by taking the average of the rates at the start and end of each 24 hour period. The 5000 l. total could be plus or minus about 200 l. at a maximum.)

After this prolonged extraction, the creosote-emulsion was allowed to settle for several days, and then the supernatant water was carefully decanted. The remaining creosote-water emulsion was dried by adding and azeotropically distilling off the water. (At this point an estimated 20 ml. of creosote were lost when the concentration of benzene became too small and the mixture bumped.) The final removal of benzene was done in a rectifying column.

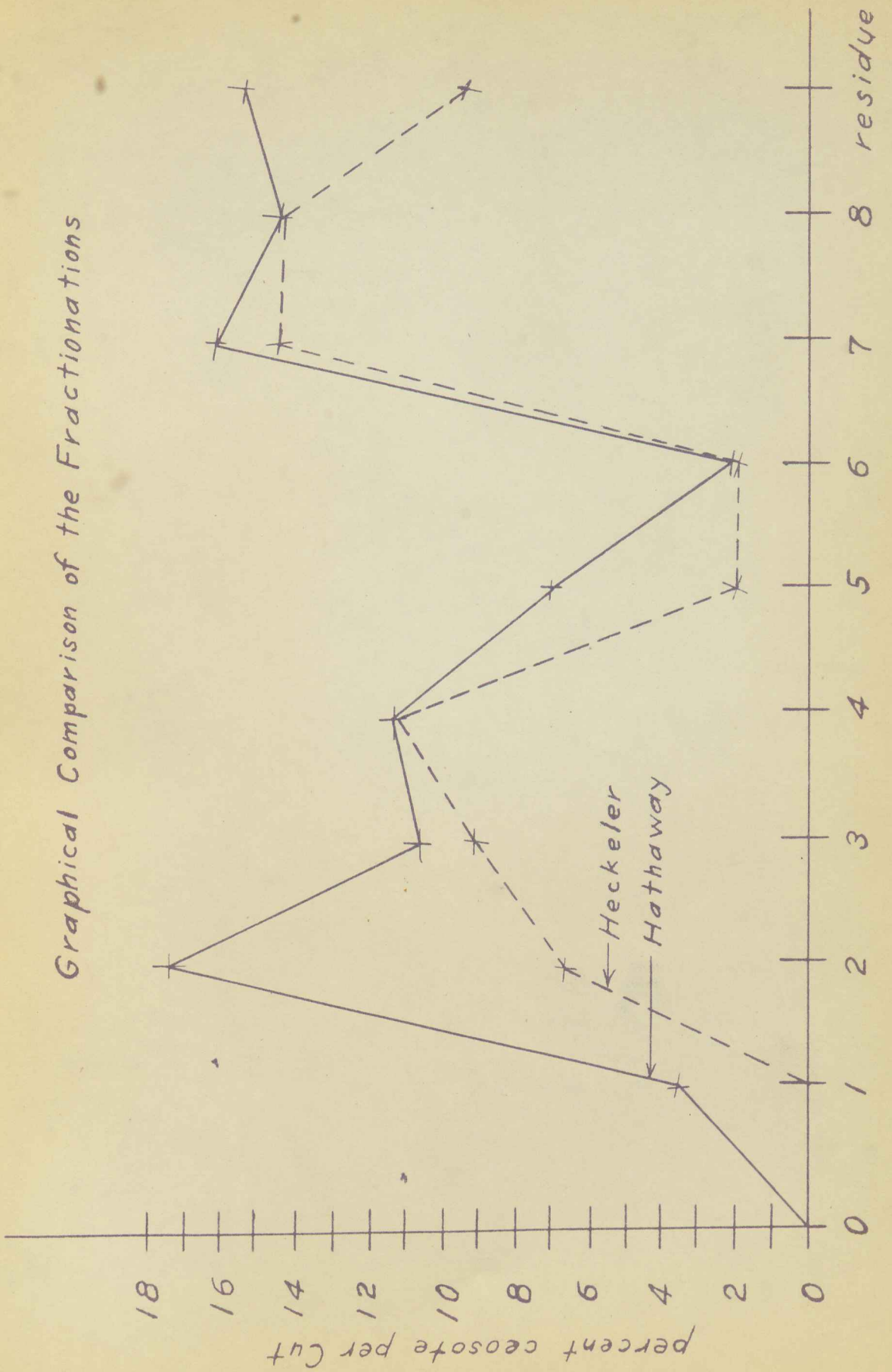
This water washed creosote was rectified through a 20 plate helice packed column which was used by Hathaway (7) for rectifying whole creosote. The volumes at each distillation range were compared with the results of Hathaway (table 1 - graph 1).

Table 1

cut no.	Heckeler			
	boiling pt. range	pressure (mm.)	volume of take-off	percent of total vol.
0-1	0-92 C.	15	0 ml.	0.0
1-2	92-95 C.	15	15 ml.	6.8
2-3	95-128C.	15	23 ml.	9.2
3-4	128-157C.	14	28 ml.	11.2
4-5	157-170C.	14	5 ml.	2.2
5-6	170-183C.	14	5 ml.	2.2
6-7	183-202C.	14	36 ml.	14.5
7-8	202-231C.	14	28 ml.	11.2
residue	over 231C.	--	23 ml.	9.2

cut no.	Hathaway				
	boiling pt. range	pressure (mm)	volume of take-off	percent of total vol.	dif. in %
0-1	0-92 C.	15	22ml.	3.6	3.6
1-2	92-105C.	15	104 ml.	17.4	11.4
2-3	105-128C.	15	64 ml.	10.7	1.5
3-4	128-152C.	15	68 ml.	11.3	0.1
4-5	152-170C.	15	42 ml.	7.0	5.0
5-6	170-163C.*	5	13 ml.	2.2	0.2
6-7	163-191C.	5	97 ml.	16.2	1.7
7-8	191-225C.	5	88 ml.	14.6	3.4
residue	over 225C.	--	108 ml.	15.5	6.3

* Pressure changed from 15 to 5 mm.


Graphical Comparison of the Fractionations
percent creosote per Cut
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8 residue
Cut Number
Heckeler
Hathaway

Results of the Leaching experiment:

300 g. of creosote were weighed out for this experiment. This weight is equivalent to 270 ml. (density of creosote is 1.08 g. per ml.), of which 20 ml. were lost as stated on page 7, which were believed to be an equivalent part of the entire water extracted creosote.

81 ml., or 32.4%, were lost by water extraction, as only 146 ml. of the creosote were fractionated, and 23 ml. remained as residue of the 250 ml. 5 ml. of this water extracted creosote (2%) were captured by the carbon tetra chloride, so that 30.4% of the water extracted creosote must have passed through the apparatus without being captured in the carbon tetra chloride.

In the comparison of the two fractionations (see table 1), it must be remembered that Hathaway started with an initial volume of 600 ml.

B. Oxidation

For the oxidation process approximately equal volumes of creosote were weighed out accurately. These samples were then oxidized with variable amounts of oxygen by direct reaction at 60°C. at atmospheric pressure. (See page 12 for apparatus.) The amount of oxygen run into these samples was measured by a change in pressure using the perfect gas law; $pv = nRT$ or $pv = nRT$ (v, R and T are constants).

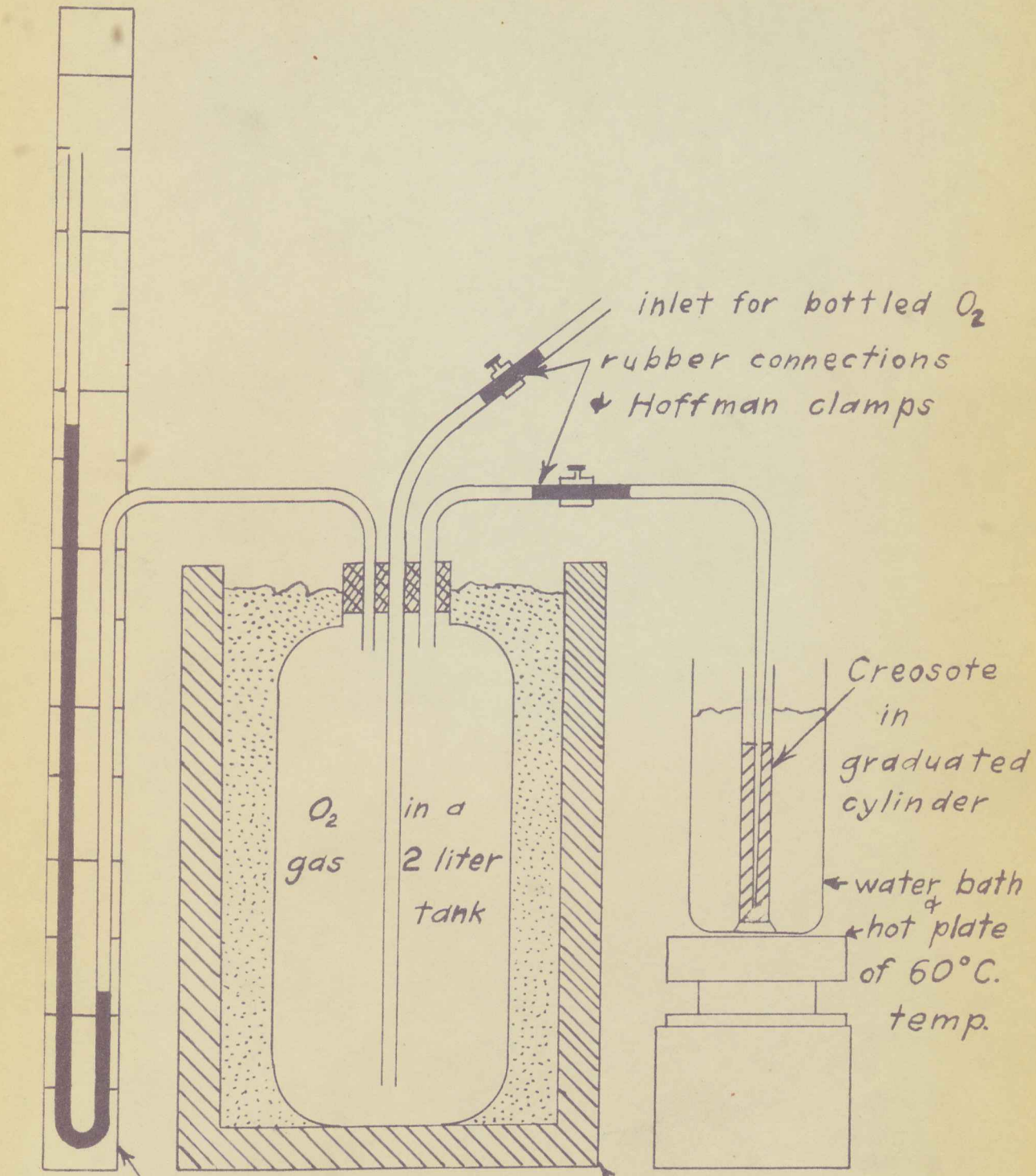
The volume of the tank used to measure the change in pressure had a volume of 2.010 liters. The oxygen was passed from the bottle into the tank and the change in pressure measured after the inlet was closed with a Hoffman clamp. The Hoffman clamp on the outlet to the creosote was then opened and the oxygen allowed to flow into the creosote. For testing the toxicity, nutrient-agar gels were used as described in the introduction.

To form these gels, 15 g. of agar and 25 g. of malt were dissolved in one liter of water. While this gel was still in the liquid state, it was placed in 500 ml. Erlemeyer flasks (100 ml. per flask). One of these flasks was the master sample,which was made by placing 5 g. of the oxidized creosote in the liquid agar. All of these flasks were then covered with aluminum foil and sterilized for a period of 15 minutes, under 15 pounds steam pressure. The master sample was then mixed completely in a Waring Blender, from which samples were pipetted to other flasks to form solutions of varied concentrations. To these flasks Lentinus Lepideus fungus (Madesin 534) was added to test for toxicity.

The fungus used for these tests was grown on nutrient-agar gels (containing no poison) in petrie dishes for a period of two weeks, in a constant temperature chamber of 28°C. "Plugs" were cut with a cork bore having a diameter of 1 cm. and placed on the

Figure 2

Oxidation Apparatus



surface of the test gels. At all times great care was taken to exclude all bacteria and fungus of the air. These test samples were then placed in the constant temperature chamber and allowed to grow for a period of three weeks, after which the growth was recorded.

Creosote was oxidized with various amounts of oxygen per gram of creosote, as shown in table 2 below.

Table 2

Samples	Pressure change of oxygen	Moles of O_2	Liters of O_2	wt. of creosote	ml. of O_2 per gm. creosote
K	406 mm.	.0452	1.01	80.22 gm.	12.5
L	739 mm.	.0814	1.83	80.60 gm.	22.6
M	1020 mm.	.1244	2.79	82.40 gm.	33.9
N	1557 mm.	.1715	3.84	81.04 gm.	47.4
O	1918 mm.	.2110	4.73	80.65 gm.	58.6
P	9398 mm.	1.0350	23.20	78.07 gm.	297.0
R*	9398 mm.	1.0350	23.20	78.68 gm.	295.0

* Samples P and R contain the same amount of oxygen, but R is a 2% hydroquinone solution of creosote, while sample P contains only creosote.

Table 3

The samples used for toxicity tests were made up with the following concentrations:

sample no.	grams of creosote in master sample	sample no.	grams of creosote in master sample
K	5.22	O	5.14
L	5.00	P	5.00
M	5.00	R	5.00
N	5.34		

sample no.	milliliters of master sample	percent creosote in agar test samples
K-.6	0.60	.0298
K-.7	0.70	.0348
K-.8	0.80	.0398
K-.9	0.90	.0443
K-1.0	1.00	.0492
K-1.1	1.10	.0547
K-1.2	1.20	.0596
L-.6	0.60	.0286
L-.7	0.70	.0334
L-.8	0.80	.0381
L-.9	0.90	.0428
L-1.0	1.00	.0476
L-1.1	1.10	.0524
L-1.2	1.20	.0572
M-.7	0.70	.0334
M-.8	0.80	.0381
M-.9	0.90	.0428
M-1.0	1.00	.0476
M-1.1	1.10	.0524
M-1.2	1.20	.0572
M-1.3	1.30	.0619
N-.7	0.70	.0356
N-.8	0.80	.0406
N-.9	0.90	.0457
N-1.0	1.00	.0508
N-1.1	1.10	.0558
N-1.2	1.20	.0610
N-1.3	1.30	.0660

Table 3 Contd.

sample no	milliliters of master sample	percent creosote in agar test samples
O-.8	0.80	.0391
O-.9	0.90	.0444
O-1.0	1.00	.0489
O-1.1	1.10	.0538
O-1.2	1.20	.0587
O-1.3	1.30	.0635
O-1.4	1.40	.0685
P- .5	0.50	.0238
P-.7	0.70	.0334
P-.8	0.80	.0381
P-.9	0.90	.0428
P-1.0	1.00	.0476
P-1.3	1.30	.0619
P-1.5	1.50	.0714
P-2.0	2.00	.0951
P-3.0	3.00	.1430
R-.5	0.50	.0238
R-.7	0.70	.0334
R-.8	0.80	.0381
R-.9	0.90	.0428
R-1.0	1.00	.0476
R-1.3	1.30	.0619
R-1.5	1.50	.0714
R-2.0	2.00	.0951
R-3.0	3.00	.1430

Results of the oxidation experiment:

It has been found most convenient to define the inhibition point in these experiments as the lowest concentration of creosote that prevents the fungus from growing on the surface of the gel. In other words, if the fungus grows on the surface of the gel, the concentration of creosote is not great enough. Formerly the inhibition point was defined as the rate of diffusion through the agar "plug".

The following table will indicate the deviation of the inhibition point (toxicity) of the creesote by addition of oxygen:

Table 4

sample no.	Types of fungus growth
K-.6	1" diameter surface growth
K-.7	1½" diameter surface growth
K-.8	inhibition point growth on top and sides of plug only
K-.9	" " " " " " " "
K-1.0	" " " " " " " "
K-1.1	" " " " " " " "
K-1.2	growth on top of plug only
L-.6	1½" diameter surface growth
L-.7	½" " " "
L-.8	inhibition point plug covered, start on surface
1-.9	growth on top of plug only
L-1.0	" " " " " "
L-1.1	" " " " " "
L-1.2	no growth on either plug or surface

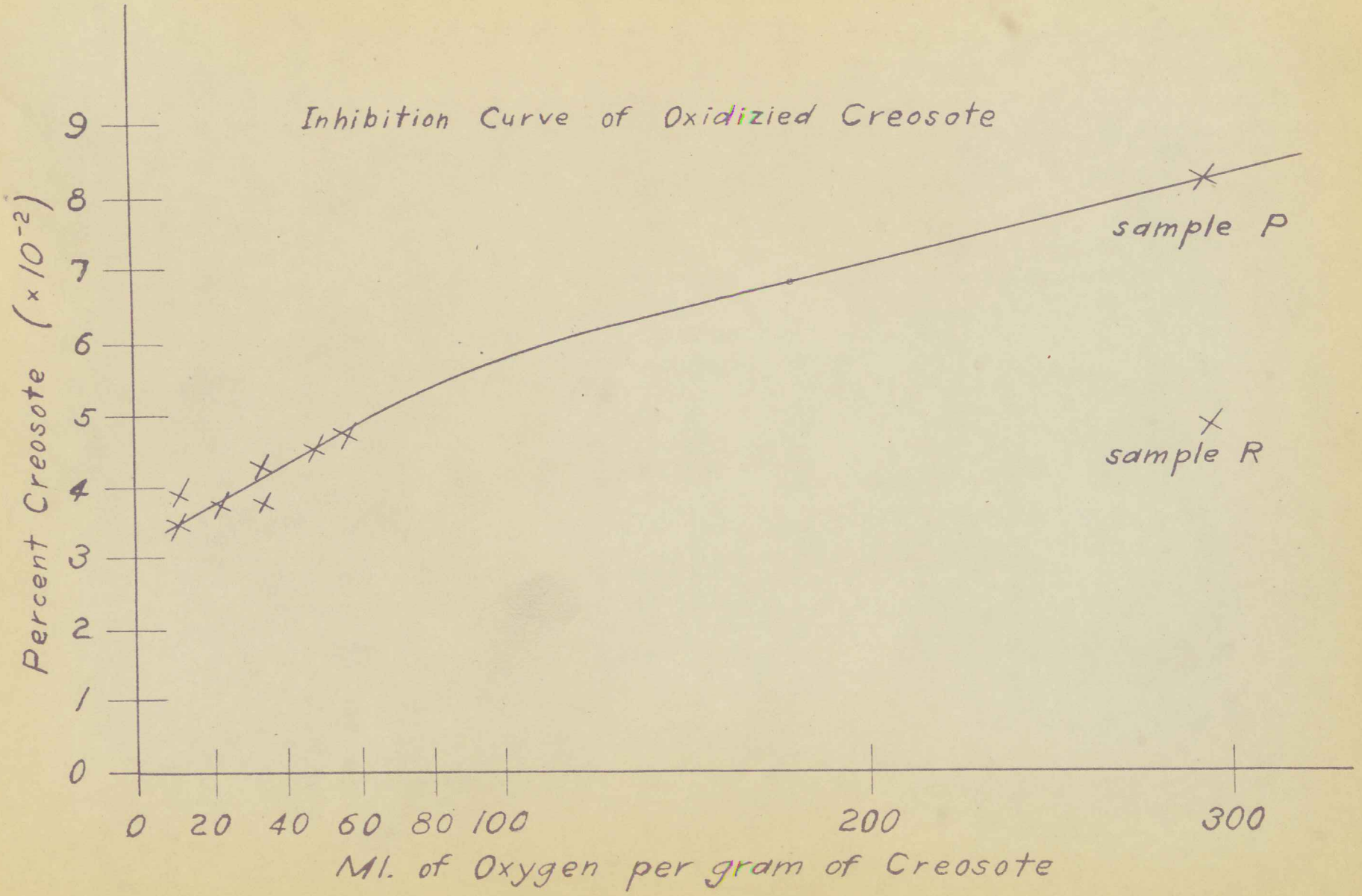
Table 4 Contd.

sample no.	Types of fungus growth
M-.7	$\frac{1}{8}$" diameter surface growth
M-.8	$\frac{1}{8}$" " " "
M-.9	inhibition point growth on top of plug only
M-1.0	" " " " " "
M-1.1	" " " " " "
M-1.2	" " " " " "
M-1.3	" " " " " "
N-.7	$\frac{1}{8}$" diameter surface growth
N-.8	small amount of surface growth
N-.9	inhibition point - start of growth on surface
N-1.0	growth on top of plug only
N-1.1	" " " " " "
N-1.2	" " " " " "
N-1.3	" " " " " "
O-.8	$1\frac{1}{8}$" diameter surface growth
O-.9	$\frac{1}{4}$" " " "
O-1.0	inhibition point - plug covered, start on surface
O-1.1	growth on top of plug only
O-1.2	" " " " " "
O-1.3	" " " " " "
O-1.4	" " " " " "

Table 4 Contd.

sample no.	Types of fungus growth
P-.5	1½" diameter surface growth
p-.7	1" " " "
P-.8	1" " " "
P-.9	1" " " "
P-1.0	½" " " "
P-1.3	½" " " "
P-1.5	½" " " "
P-2.0	inhibition point growth on top of plug only
P-3.0	" " " " " "
R-.5	2" diameter surface growth
R-.7	1½" " " "
R-.8	¼" " " "
R-.9	¼" " " "
R-1.0	inhibition point growth on top and sides of plug
R-1.3	growth on top of plug only
R-1.5	" " " " " "
R-2.0	no growth at all
R-3.0	" " " "

The effects of oxygen on the toxicity of creosote are also shown graphically on page 19 (graph no. 2).


Inhibition Curve of Oxidizied Creosote
Percent Creosote (×10⁻²)
0
1
2
3
4
5
6
7
8
9
0
20
40
60
80
100
200
300
Ml. of Oxygen per gram of Creosote
sample P
sample R

Graph 2

Discussion

From toxicity tests on the various fractions of creosote, Hathaway has found that the fractions lost by leaching were much less toxic than those which were unaffected by water. Weeks (9) ran toxicity tests on both pure creosote and water extracted creosote and found no difference in their toxicities (using the wood block method). It would seem, therefore, that the fractions lost by leaching were probably those basic and acidic compounds which have little effect on the toxicity. With further study and different solvents to replace the carbon tetra chloride, a much more complete picture of leaching might be seen.

Since the amount of vaporization during the oxidation process was not measured, and since the extent of reaction was not certain, it was felt that the perfect gas law was accurate enough for measuring the oxygen. From the results as shown by graph 2 (page 19) it would seem that the initial oxygen had the greatest influence in the decrease in toxicity, but since no maximum is shown, therefore, it is believed that further data would show that the toxicity would be decreased indefinitely by additional oxygen. It must be remembered that the amounts of oxygen used in this experiment were small, as compared to natural conditions, and further study might prove to be of value. The effects of oxidation are best shown by samples P and R, where sample P contains pure creosote and R is a 2% solution of hydroquinone. It would be advisable, in case of further study, to use an oxidation inhibitor other than hydroquinone, as hydroquinone is not too soluble in creosote (even to the extent of a 2% solution).

Summary

1. Water has little effect on the toxicity of creosote. When water does wash away almost 1/3 of the creosote, it does not change the toxicity, as this material lost is made up of low boiling hydrocarbons, acidic compounds and basic compounds which have little affect of toxicity.

2. Oxygen (or oxidation) decreases the toxicity of creosote. While the initial oxygen shows the greatest decrease, there is no maximum in the toxicity curve and oxygen is a definite factor in the weathering of creosote.

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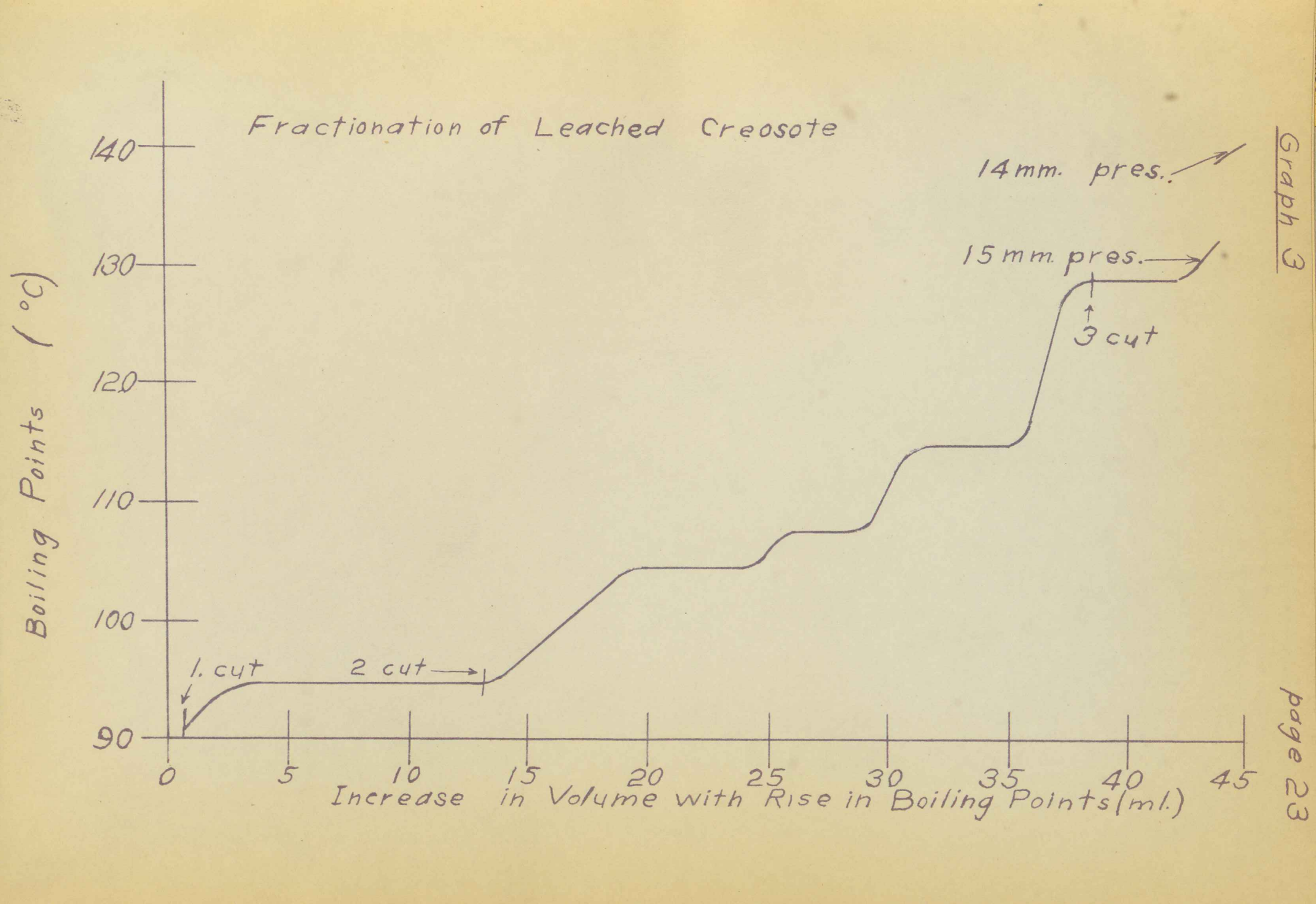
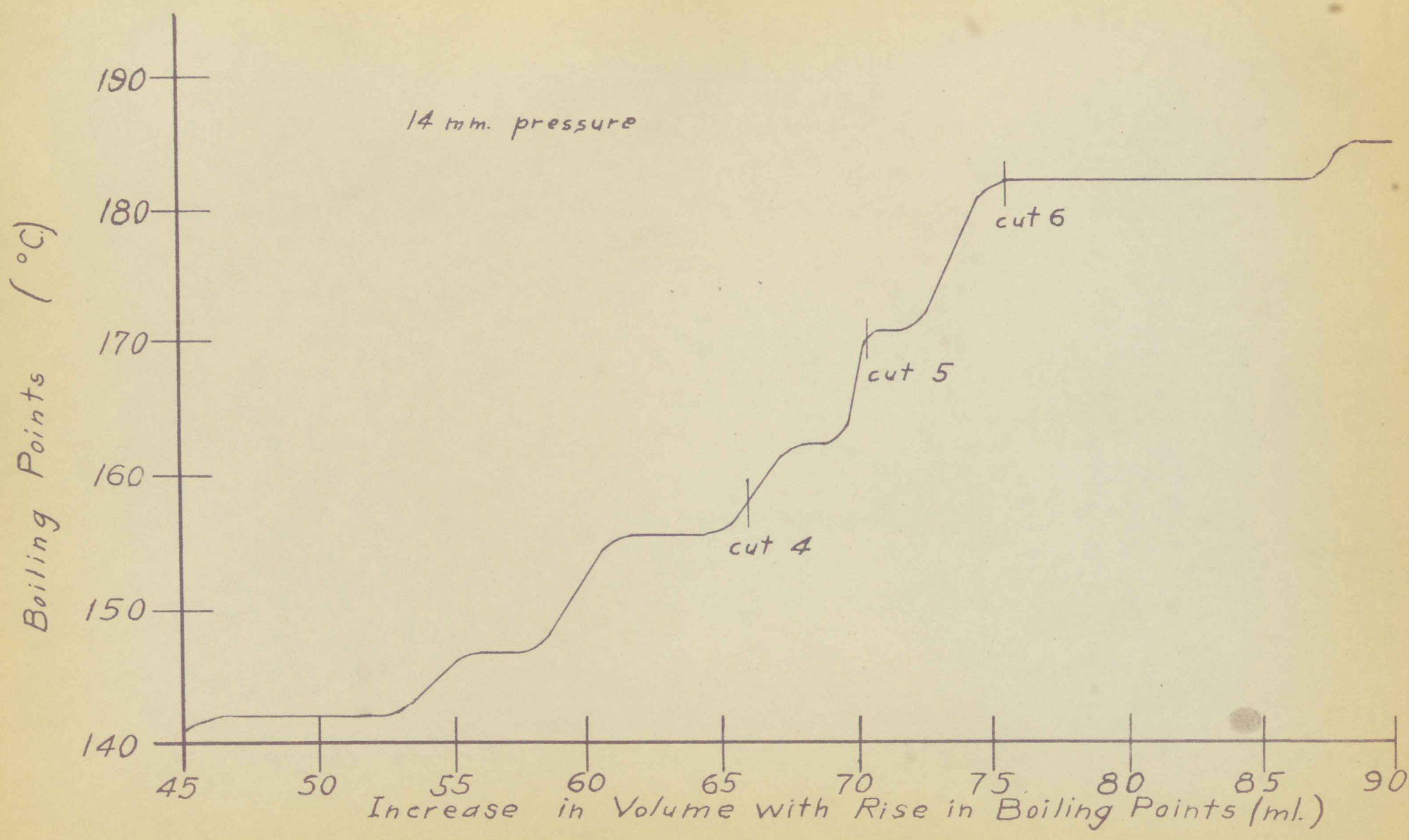
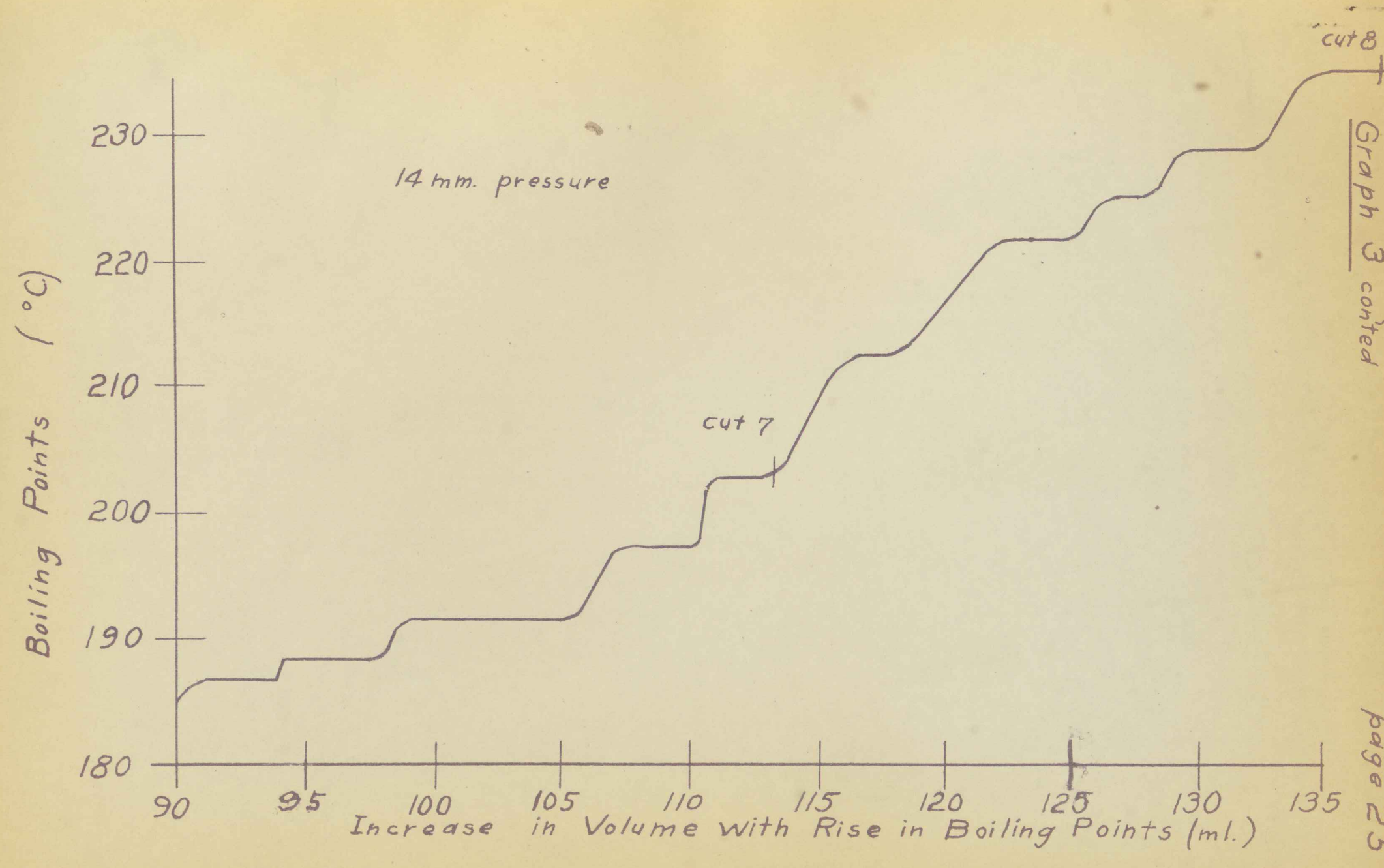

Fractionation of Leached Creosote
Graph 3
14mm. pres.
15 mm. pres.
3 cut
1. cut
2 cut
Boiling Points (°C)
140
130
120
110
100
90
0
5
10
15
20
25
30
35
40
45
Increase in Volume with Rise in Boiling Points (ml.)


14 mm. pressure
Boiling Points (°C.)
190
180
170
160
150
140
cut 6
cut 5
cut 4
45
50
55
60
65
70
75
80
85
90
Increase in Volume with Rise in Boiling Points (ml.)


Graph 3 cont'ed
cut 8
14 mm. pressure
cut 7
Boiling Points (°C)
230
220
210
200
190
180
90
95
100
105
110
115
120
125
130
135
Increase in Volume with Rise in Boiling Points (ml.)